NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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PROPOSED LETTER TO THE EDITOR

VISIBLE ABSORPTION SPECTRA OF Li, Na, AND

K IN MOLTEN LiCl-KCl

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INTRODUCTION

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In order to elucidate the nature of the species formed upon the addition of an alkali metal to an alkali halide melt, the absorption spectra obtained upon the addition of Li, Na, and K to molten LiCl-KCl were measured. The eutectic mixture of LiCl and KCl was used in order that the measurements be made at as low a temperature as possible. Although the attack of heated alkali metal vapors has restricted the use of silicate containers in such work, it was not found to be a primary problem. The reaction of an alkali metal with the quartz curvettes was minimized by using anhydrous salts and by affording the metal sample opportunity to go into solution rather than react with the container upon heating. The absorption spectra obtained can all be characterized by a band with a peak maximum at 530 mμ.

Experimental

Quartz cuvettes, 1 centimeter in diameter, were used as containers. Although heated alkali metal vapors react with silicates, it was found that if the salts were anhydrous, the alkali metal would dissolve in the salt without discoloring that portion of the cell containing the melt.

However, there were irreversible losses of alkali metal vapor due to reaction with water on the container walls[1] and with the glass cuvette itself. This resulted in a continued decrease in the absorption band.

The cells were wrapped with Inconel heating strips and placed in an insulating container. The steady-state temperatures were controlled by means of a Variac to within ±5° C. The temperature of the system was measured by means of a platinum - 13 percent rhodium thermocouple. All measurements were made at 400° C.

The spectra were obtained by use of a Beckman DK, double-beam, recording spectrophotometer. Each metal-salt mixture was compared to air in the reference compartment. The baseline for the system was obtained by running the spectrum of the salt mixture along when all the metal had left the system. In this way the problems in reproducing the exact temperature, concentration, and configuration of the sample cell were eliminated. The results obtained essentially enabled us to calculate a spectrum of the metal-salt system as compared to the identical salt system.

The standard preparation of molten salt halides was found to have inherent difficulties. If the salt were melted in vacuum, washed with the appropriate halide gas, then with a dry inert gas, and filtered through Pyrex glass wool, it was found that not all hydrolysis products were removed and that often residual amounts of halogen gas reacted with the alkali metals added. In order to overcome the difficulties produced by heating the salt in the presence of water and by introducing halogen

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[1] I. Warshawsky, J. Inorg. Nucl. Chem. 25 (919) 1963.

gases into the system, a new purification technique was used.[2] It was

found that anhydrous salts could be obtained by washing with liquid

ammonia. This procedure eliminated the possibility of hydrolysis since

the salt was not heated until all the water was removed. This pro-

cedure also eliminated the use of halide and halogen gases.

Preparation of Metal-Molten Salt Solutions

Reagent grade LiCl and KCl were weighed out after vacuum drying to

form the eutectic mixture (59 M percent LiCl). Removal of water from

the salts was then done by washing with dry liquid ammonia. A system

shown in Fig. 1 was used first to purify the salt mixture and then to

prepare the metal-salt solution. After repeatedly washing the salt

mixture in region B, and pumping on the washed salt to remove residual

ammonia, the potassium, and also the sodium, was distilled from region A

into region C. The system was then sealed off at D while pumping. The

salt mixture in region B was easily transferred into region C by tipping

the ampule and transferring the finely divided solid without heating.

A heater was then placed about the cell and the solution formed by

melting the eutectic mixture.

Since lithium badly discolored the cuvette upon heating, it was

necessary to alter the previous procedure. This was done by carrying

the lithium metal over in a diffusion stream of ammonia into the salt

in region B rather than into the cuvette at C. The lithium metal-

eutectic salt mixture was then transferred into region C. This method

[2]I. Warshawsky and J. Greenberg, J. Inorg. and Nuclear Chem.,
(In Press).

eliminated a coating of lithium metal from being present on the walls
of the quartz cuvette. The process involved placing lithium in a side
arm and dissolving it in liquid ammonia. A dry ice-acetone bath was
placed around region B, which contained the salt, and the ammonia with
lithium dissolved in it was distilled onto the salt. This process
resulted in lithium metal being introduced into the water-free salt.
The residual ammonia was removed by pumping. The system was sealed
off and the metal-salt mixture was transferred into region C. The metal-
salt solution was formed by heating the salt without any discoloration
of the glass at the glass-liquid interface.

The amount of sodium or potassium introduced into the salt was
estimated by reacting similar amounts of metal as used with the salt
mixtures with water vapor and measuring the pressure of hydrogen
evolved. Initial concentrations of metal were thus estimated to be
$<10^{-5}$ mole of alkali metal.

RESULTS

The absorption spectra obtained with the addition of Li, Na, or K
to LiCl-KCl eutectic mixture can be characterized by a single visible
band with a peak maximum at about 530 mμ. No additional bands or
structures were observed in the range 3000 to 15,000 A^o. The concentra-
tion of the alkali metal in the salt could not be kept at a constant value.
The loss of alkali metal was primarily due to reaction with water on the
cuvette walls since the discoloration of the cuvette due to the alkali
metal attack was minimal. Once the solution had been formed (i.e. the
salt melted with the metal in it), spectral readings during the first

that the absorbing species in each case is the same. If we, therefore, assume a behavior similar to that which has been observed in the solid, then the absorbing species in the melt will be a "trapped" or solvated electron.

It is of interest, therefore, to compare the oscillator strength of an electron trapped in the solid with the oscillator strength of the proposed electron in the melt. Since we have only an order of magnitude estimate of the metal concentration and since the equation[4] used involves the refractive index of the solid salt and complex polarizability of the electron in a solid, we can only estimate that the oscillator strength is less for the molten system than the solid. This can be interpreted as indicating an interaction of the electron with the ions surrounding it.

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[4]F. Seitz, "Modern Theory of Solids," (McGraw-Hill Book Co., New York, 1940), p. 665.

15 minutes indicated at least a 60 percent decrease in the concentration

of alkali metal. Since the initial alkali metal addition was estimated

to be 10^{-5} mole, the concentration after 15 minutes was considered to

be of the order of 10^{-6} mole of metal. The liquid volume of the salt

was approximately 10 cc with the result that the concentration of metal

in the salt was estimated to be 10^{-7} mole/cc. The data observed for the

absorption band of Li, Na, and K in LiCl-KCl are given in Fig. 2. The

test conditions were as follows:

Temperature, °C . . . . 400 ±5
Position of bond peak, mμ . . . . 530 (2.34 ev)
Half-width, $\Delta v_{1/2}$, mμ . . . . 465-585 (0.54 ev)
Metal concentration, mole/cc . . . . 10^{-7}

DISCUSSION

The presence of a distinct visible band rather than a continuum

indicates that the energy level structure typical of the metallic state

is not present. The fact that Li, Na, and K all produced the same ab-

sorption pattern indicates that the absorbing species could not be a

distinct metal atom. The spectra of Li in LiCl at 650° C have been re-

ported to have a band maximum at 550 mμ.[3] It is also stated that the

absorbing species of the melt cannot be assumed to be an excited alkali

metal atom. When alkali metals are added to alkali halide crystals, the

absorbing species is considered to be a "trapped" electron or F center.

The addition of various alkali metals to a particular alkali halide

crystal will produce similar spectra. Since the peak position and band

shape of Li, Na, and K in molten LiCl-KCl are the same, it can be assumed

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[3] J. P. Young, J. Phys. Chem. **67** 2507 (1963).

To Vacuum

(Also inlet for liquid NH_3)

Graded
seal
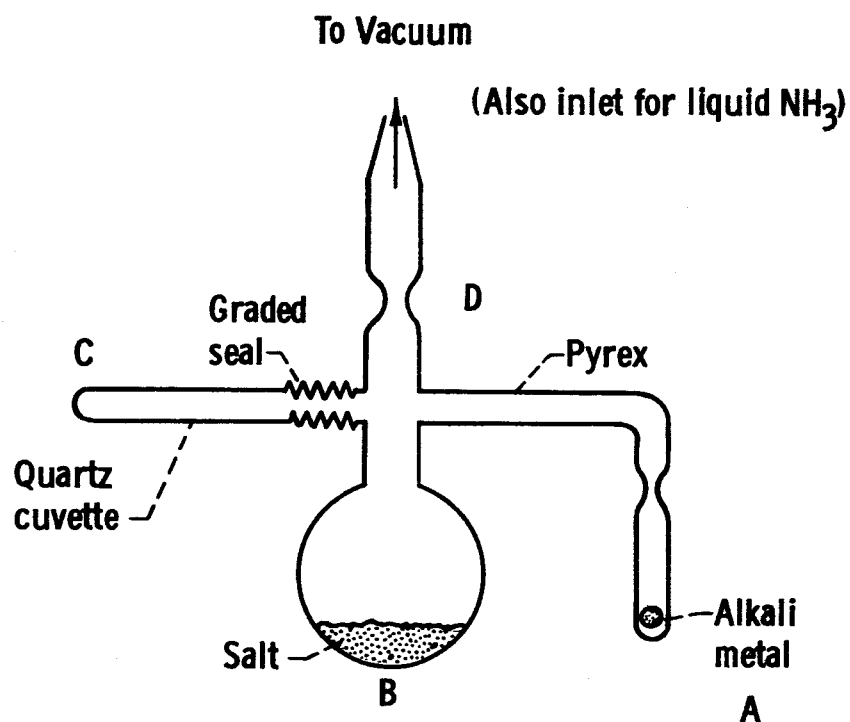
C

D

Pyrex

Quartz
cuvette

Salt

Alkali
metal

B

A

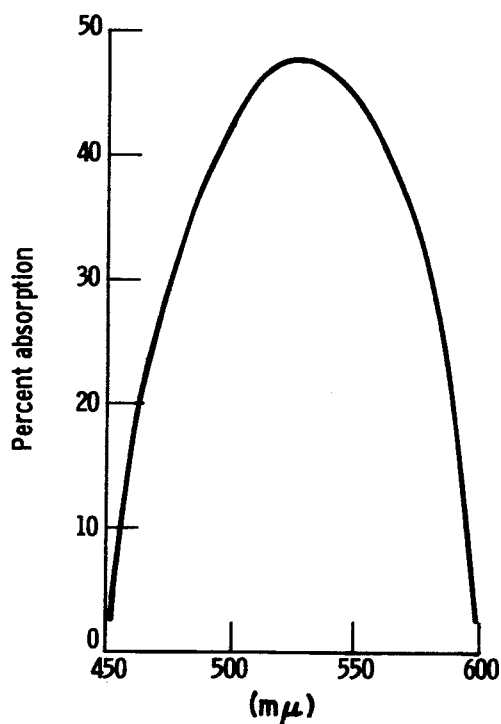Fig. 1. – Apparatus for preparation of metal-salt system.

Fig. 2. – Absorption spectra of
~10^{-7} mole/cc of Li, Na, and K in
LiCl-KCl.